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(54)【発明の名称】 ガラスセラミックス複合電解質、及びリチウム二次電池

(57)【要約】

【課題】 媒体中に非水系電解液を含浸してなる電解質において、高いイオン伝導性を有し、かつ厚みを薄くした場合においても十分な機械的強度を有する電解質、および電池容量が高く、充放電サイクル特性も良好で、長期的に安定して使用できるリチウム二次電池を提供する。

【解決手段】 リチウムイオン伝導性のガラスセラミックス粉体を含有する媒体中に非水系電解液を含浸してなるガラスセラミックス複合電解質、およびその複合電解質と、正極、負極、とを備えたリチウム二次電池。ガラスセラミックス粉体は平均粒径2.0μm以下(体積分率)、かつ最大粒径が4.4μm以下であり、リチウムイオン伝導度 $1 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ 以上の粒子からなる。ガラスセラミックス複合電解質の厚さは100μm以下であり、リチウムイオン伝導度は $1 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ 以上である。

【特許請求の範囲】

【請求項1】 リチウムイオン伝導性のガラスセラミックス粉体を含有する媒体中に非水系電解液を含浸してなるガラスセラミックス複合電解質。

【請求項2】 該ガラスセラミックス粉体は平均粒径 $20\mu\text{m}$ 以下（体積分率）、かつ最大粒径が $44\mu\text{m}$ 以下であり、リチウムイオン伝導度 $1 \times 10^{-4}\text{S} \cdot \text{cm}^{-1}$ 以上の粒子からなる請求項1記載の複合電解質。

【請求項3】 該媒体はシート状高分子材料にガラスセラミックス粉体を含有してなる請求項1又は2記載の複合電解質。

【請求項4】 厚さ $100\mu\text{m}$ 以下であり、イオン伝導度 $1 \times 10^{-5}\text{S} \cdot \text{cm}^{-1}$ 以上である請求項1から3のうちのいずれか一項記載の複合電解質。

【請求項5】 該媒体中におけるガラスセラミックス粉体の含有量が $10 \sim 90$ 質量％である請求項1から4のうちのいずれか一項記載の複合電解質。

【請求項6】 正極、負極、及びセパレータを備えたリチウム二次電池であって、該セパレータは請求項1から5のうちのいずれか一項記載の複合電解質からなるリチウム二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、リチウムイオン伝導性のガラスセラミックス粉体を含有する複合電解質に関する。更に、本発明はこの複合電解質を備えたリチウム二次電池に関する。

【0002】

【従来の技術】 従来から、電池における電解質としては、一般に水系或いは非水系の電解液が使用されていたが、近年、このような液体が中心の電解質に替わり、高分子で構成されたポリマー電解質を用いたリチウム二次電池が注目されるようになった。

【0003】 すなわち、このようにポリマー電解質を用いたリチウム二次電池においては、ポリマー電解質中に液体の電解液が保持されるため、漏液しにくく、腐食性も少なく、電池の構造が簡単でその組立ても容易になる等の利点があった。

【0004】 ここで、このようなポリマー電解質は電解液のみに比べ、リチウムイオンの伝導性が低いため、このポリマー電解質の厚みを薄くすることが行なわれるようになった。しかし、このようにポリマー電解質を薄くした場合その機械的強度が低くなって、電池の作製時にこのポリマー電解質が破壊され、正極と負極とが短絡し易いという問題があった。

【0005】 そこで、従来においては、特開平6-140052号公報等示されるように、電解質中にアルミナ等の無機酸化物を添加して複合電解質とし、機械的強度を向上させることが提案された。アルミナ以外にもシリカやアルミン酸リチウム等の無機酸化物が提案されている。し

かし、アルミナ等の無機酸化物を電解質中に添加させると、複合電解質におけるリチウムイオンの伝導性が大きく低下する問題がある。また、この複合電解質を備えたリチウム二次電池において充放電を繰り返して行なうと、電解質と上記の無機酸化物とが反応して、リチウム二次電池における充放電サイクル特性が大きく低下してしまう。

【0006】

【発明が解決しようとする課題】 本発明は、媒体中に非水系電解液を含浸してなる電解質において、高いイオン伝導性を有し、かつ厚みを薄くした場合においても十分な機械的強度を有する電解質を提供することを目的とする。また、本発明は、非水系電解液を含浸してなる電解質をセパレータとして備えたリチウム二次電池において、電池容量が高く、充放電サイクル特性も良好で、長期的に安定して使用できるリチウム二次電池を提供することをもう一つの目的とする。

【0007】

【課題を解決するための手段】 本発明者らは、電解質中に種々の充漬物を添加して詳細な実験を行った結果、特定の組成のガラスセラミックス粉体を非水系電解液と共にポリマー媒体中に分散・含有させたガラスセラミックス複合電解質は、従来のリチウムイオンの伝導性を示さない無機酸化物を含んだ複合電解質に比べて著しく高いリチウムイオンの伝導性を示すことを見出した。また、ここで得られた複合電解質をリチウム二次電池に適用すると、従来のリチウムイオン伝導性を示さない無機酸化物を含んだ複合電解質をリチウム二次電池に適用した場合に比べて電池容量が高く、充放電サイクル特性も著しく向上することを発見し、本発明をなすに至った。

【0008】 すなわち、本願の請求項1に記載の発明は、リチウムイオン伝導性のガラスセラミックス粉体を含有する媒体中に非水系電解液を含浸してなるガラスセラミックス複合電解質であり、請求項2に記載の発明は、該ガラスセラミックス粉体は平均粒径 $20\mu\text{m}$ 以下（体積分率）、かつ最大粒径が $44\mu\text{m}$ 以下であり、リチウムイオン伝導度 $1 \times 10^{-4}\text{S} \cdot \text{cm}^{-1}$ 以上の粒子からなる請求項1記載の複合電解質であり、請求項3に記載の発明は、該媒体はシート状高分子材料にガラスセラミックス粉体を含有してなる請求項1又は2記載の複合電解質であり、請求項4に記載の発明は、厚さ $100\mu\text{m}$ 以下であり、イオン伝導度 $1 \times 10^{-5}\text{S} \cdot \text{cm}^{-1}$ 以上である請求項1から3のうちのいずれか一項記載の複合電解質であり、請求項5に記載の発明は、該媒体中におけるガラスセラミックス粉体の含有量が $10 \sim 90$ 質量％である請求項1から4のうちのいずれか一項記載の複合電解質であり、請求項6に記載の発明は、正極、負極、及びセパレータを備えたリチウム二次電池であって、該セパレータは請求項1から5のうちのいずれか一項記載の複合電解質からなるリチウム二次電池である。

【0009】そして、本発明の複合電解質は、リチウムイオン伝導性の電解質中にリチウムイオン伝導性のガラスセラミックス粉体を含有させることにより、電解質におけるリチウムイオンの伝導性が低下するということが少なく、電解質の機械的強度が向上され、さらに電池容量、特に充電容量も高くできる。

【0010】また、上記のガラスセラミックス粉体は反応性が低いため、充電時に電解液とこのガラスセラミックスとが反応するということが少なくなり、従来のアルミナ等の無機酸化物を添加した電解質のように電解質が反応してリチウム二次電池の充電サイクル特性が低下するということも少なくなる。

【0011】本発明の複合電解質は電池として使用した場合、薄い方が電池の単位体積当たりの電極面積が広く確保できるため高容量の電池が得られる。そこで、本発明の複合電解質は厚さが100 μm 以下のシート状が好ましい。また、本発明の複合電解質において、ガラスセラミックス粉体は媒体中に均一に分散されていることが、複合電解質のイオン伝導性、及び機械的強度の面で好ましい。分散性を良好にするために、ガラスセラミックス粉体の粒径は、平均で20 μm 以下が好ましく、10 μm 以下がより好ましい。最大粒径としては44 μm 以下が好ましい。

【0012】リチウムイオン二次電池の充電時におけるリチウムイオンの移動性は、電解質のリチウムイオン伝導性に依存するため、本発明の複合電解質のリチウムイオン伝導度は高い方が好ましい。具体的には、 $1 \times 10^{-5} \text{S} \cdot \text{cm}^{-1}$ 以上であることが好ましく、 $1 \times 10^{-4} \text{S} \cdot \text{cm}^{-1}$ 以上であることがより好ましい。ゲル状の固体電解質のイオン伝導度は電解液自体のリチウムイオン伝導度よりも一般には低い。また、ゲル状の固体電解質に機械的強度を増すために無機酸化物を添加する場合、添加材自体のリチウムイオン伝導性が低いと、電解質のイオン伝導性は更に低下するのが一般的である。ところが、添加材としてリチウムイオン伝導性のガラスセラミックス粉体を用いると、電解質のリチウムイオン伝導性の低下を防止する効果があり、結局、高いイオン伝導度と、十分な機械的強度を有する複合電解質を得ることができる。本発明の複合電解質において、添加材としてのガラスセラミックス粉体は、複合電解質のリチウムイオン伝導度よりも高いリチウムイオン伝導度のガラスセラミックス粒子からなることが望ましい。具体的には、ガラスセラミックス粉体を構成するガラスセラミックス粒子のリチウムイオン伝導度は、好ましくは $1 \times 10^{-5} \text{S} \cdot \text{cm}^{-1}$ 以上であり、より好ましくは $1 \times 10^{-4} \text{S} \cdot \text{cm}^{-1}$ 以上である。

【0013】本発明の複合電解質を構成する媒体は、電池として用いた時の体積当たりの電池容量を大きくできるとともに、可塑性を有し様々な形状に成形が可能である点から、シート状高分子材料にガラスセラミックス粉体を含有してなることが好ましい。また、本発明の複合

電解質を構成する媒体は、非水系電解液を会浸してゲル状物となるよう、微細な孔を有する多孔質体であることが好ましい。

【0014】本発明の複合電解質を構成するシート状高分子材料としては、ポリエチレン、ポリプロピレン等のポリオレフィン、ポリテトラフルオロエチレン、ポリクロロトリフルオロエチレン、ポリビニルデンフルオリド等のフッ素樹脂、ポリアミド類、ポリエステル類、ポリアクリレート等の高分子材料を用いることができる。媒体の材料としては、電解液を安定して会浸させることができること、加工性が良好であること、可塑性に優れること、ガラスセラミックスとの相性が良く高いイオン伝導性を示すこと等が要求される。これらの性質をバランスよく備えたものとして、特にフッ素樹脂が好ましい。

【0015】また、本発明の複合電解質において非水系電解液を構成する溶質としては、例えば、ヘキサフルオロリン酸リチウム(LiPF₆)、テトラフルオロボウ酸リチウム(LiBF₄)、過塩素酸リチウム(LiClO₄)、ヘキサフルオロヒ酸リチウム(LiAsF₆)、トリフルオロメタンスルホン酸リチウム(LiCF₃SO₃LiClO₄)、トリフルオロメタンスルホン酸イミドリチウム(LiN(CF₃SO₂)₂)等のリチウム化合物を用いることができる。さらに、上記の溶質の溶媒としては、例えば、エチレンカーボネート、プロピレンカーボネート、ブチレンカーボネート、ジメチルカーボネート、ジエチルカーボネート、γ-ブチロラクトン、スルホラン、1,2-ジメトキシエタン、ジメチルエーテル、アセトニトリル等の有機溶媒を使用することができる。上記の溶質を上記溶媒に溶解して非水系電解液とし、本発明の複合電解質に使用することができる。本発明の複合電解質はゲル状であることが好ましい。複合電解質をゲル状にすることにより、非水系電解液を高濃度に安定して会浸させることができ、高いイオン伝導性を発現することができる。これらの非水系電解液を用いることにより、本発明の複合電解質をゲル状とすることができる。

【0016】ここで、上記のように電解質中に高いイオン伝導度を有するリチウムイオン伝導性のガラスセラミックス粉体を含有させる際、その量が少なすぎると、複合電解質のリチウムイオン伝導度の向上がみられず、また複合電解質における強度を十分に向上させることができない。一方、その量が多くなりすぎると電解液の含有量が少なくなるため、複合電解質および上記のガラスセラミックス粉体と電極との接触がほとんど固体同士となるため接触性が悪くなって電極と複合電解質及び上記のガラスセラミックス粉体の間におけるリチウムイオンの移動性が悪くなる。そこで、本発明の複合電解質において、媒体中におけるリチウムイオン伝導性ガラスセラミックス粉体の含有量の下限としては10質量%以上が好ましく、20質量%以上がより好ましい。また、上限としては90質量%以下が好ましく、80質量%以下がより好

ましい。

【0017】本発明の複合電解質は、リチウムイオン伝導性のガラスセラミックス粉体を含有する。このガラスセラミックス粉体は主結晶相が $Li_{1+x}yAl_xTi_{12-x}Si_yP_3-yO_{12}$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$) のガラスセラミックスからなることが好ましい。このガラスセラミックス粉体は、 $Li_{20}Al_{120}P_{20}Ti_{102}Si_{102}$ -P205系の組成の母ガラスを熱処理して、主結晶相を $Li_{1+x}yAl_xTi_{12-x}Si_yP_3-yO_{12}$ として結晶化させ、その後、粉砕することにより得ることができる。主結晶相 $Li_{1+x}yAl_xTi_{12-x}Si_yP_3-yO_{12}$ のパラメータとして、好ましくは、 $0 \leq x \leq 1$, $0 \leq y \leq 1$ であり、より好ましくは、 $0 \leq x \leq 0.4$, $0 < y \leq 0.6$ である。また、母ガラスの酸化物換算の組成比としては、mol%表示で、 Li_{20} は12~18%、 Al_{20} は5~10%、 Ti_{102} は35~45%、 Si_{102} は1~10%、 P_{205} は30~40%であることが好ましい。この組成範囲の場合、溶融ガラスをキャストして容易にガラスを得ることができ、この母ガラスを熱処理して得られる上記結晶相をもつガラスセラミックスは高いリチウムイオン伝導性を有する。

【0018】本発明のリチウム二次電池は正極、負極、及びセパレータとしてガラスセラミックス複合電解質を備える。本発明のリチウム二次電池において、その正極に使用する材料としては、リチウムの吸蔵、放出が可能な遷移金属化合物を主成分として用いることができる。例えば、マンガーン、コバルト、ニッケル、バナジウム、ニオブ、モリブデン、チタン等の遷移金属とリチウムを含む遷移金属化合物を主成分として使用することができる。特に、主成分としてコバルト酸リチウムを含有する正極が、高起電力、サイクル特性の点で優れる。

【0019】また、本発明のリチウム二次電池において、その負極に使用する材料としては、金属リチウムやリチウムの吸蔵、放出が可能な合金、酸化物及びカーボン材料等を使用することができる。

【0020】

【発明の実施の形態】以下、本発明に係る複合電解質、及びこれを備えたリチウム二次電池について、具体的な実施例を挙げて説明すると共に、比較例を挙げ本発明に係る複合電解質、及びこれを備えたリチウム二次電池が優れている点を明らかにする。なお、本発明は下記の実施例に示したものに限定されるものではなく、その要旨を変更しない範囲において適宜変更して実施できるものである。

【0021】（実施例1）

リチウムイオン伝導性ガラスセラミックス粉体の作製原料として $NH_4H_2PO_4$ 、 $Al(P_2O_5)_3$ 、 Li_2CO_3 、 SiO_2 、 TiO_2 を使用し、これらを酸化物換算のmol%で P_{205} を35.0%、 Al_{20} を7.5%、 Li_{20} を15.0%、 Ti_{102} を38.0%、 Si_{102} を4.5%といった組成になるように秤量して均一に混合した後に、白金ボットに入れ、電気炉中1500℃でガラス融液を攪拌しながら2時間加熱溶解した。その後、ガラス融液を水中

に直接キャストし、母ガラスを得た。この母ガラスを950℃で12時間の熱処理を行うことにより、目的のガラスセラミックスを得た。析出した結晶相は粉末X線回折法により、 $Li_{1+x}yAl_xTi_{12-x}Si_yP_3-yO_{12}$ ($0 \leq x \leq 0.4$, $0 < y \leq 0.6$) が主結晶相であることが確認された。そのガラスセラミックスのイオン伝導度は、25℃の室温において $1.4 \times 10^{-3} S \cdot cm^{-1}$ であった。このガラスセラミックスを、遊星ボールミルを用いて粉砕した後に分級を行ない、平均粒径7 μm のリチウムイオン伝導性ガラスセラミックス粉体を得た。

【0022】媒体の作製

ポリビニリデンフルオライド (PVDF) とヘキサフルオロプロピレン (HFP) および上記リチウムイオン伝導性ガラスセラミックスのそれぞれの粉体を35:40:25の質量比でアセトンに20質量%投入し、アセトン懸濁液を調製した。この液をキャスト法により成膜した後、真空乾燥させて厚さ50 μm のシート状ガラスセラミックス複合媒体を作製した。

【0023】非水系電解液の調製

エチレンカーボネート (EC) とジメチルカーボネート (DMC) を50:50の質量比で混合した溶媒にヘキサフルオロリン酸リチウム ($LiPF_6$) を1mol/Lの濃度で溶解して、非水系電解液とした。

【0024】複合電解質の作製

上記ガラスセラミックス複合媒体を、室温で上記非水系電解液に10分間浸漬することによって、ゲル状物からなるシート状の複合電解質を得た。

【0025】イオン伝導度の測定

この得られた複合電解質を2枚のステンレスシートで挟み込み、これらのステンレスシートを電極として、リチウムイオン伝導度測定用の試料を作製した。室温におけるインピーダンス測定を行ない、イオン伝導度を求めた結果、イオン伝導度は、 $3.1 \times 10^{-4} S \cdot cm^{-1}$ であった。

【0026】（比較例1）媒体の作製時に、リチウムイオン伝導性ガラスセラミックスの替わりに、表面修飾されたフェムドシリカ (SiO_2) を同量加えたこと以外は、実施例1と同様にシート状複合電解質を作製し、同様にイオン伝導度を求めた。その結果、イオン伝導度は、 $1.7 \times 10^{-4} S \cdot cm^{-1}$ であった。実施例1と比較例1を比較すると、それぞれの複合電解質膜のイオン伝導度は2倍近く実施例1の方が高い結果となった。これはイオン伝導性ガラスセラミックスを含有した効果である。

【0027】（実施例2）次に、正極、負極、及びセパレータとしてガラスセラミックス複合電解質とを備えたリチウム二次電池の作製例を説明する。

【0028】正極の作製

正極の作製には、正極材料として市販のコバルト酸リチウム ($LiCoO_2$)、導電剤としてアセチレンブラック、結着剤としてフッ素樹脂粉末 (ポリビニリデンフルオライド (PVDF)) を用いた。質量比で92:10:8のコバルト酸

リチウム、アセチレンブラック、及びポリビニリデンフルオライドを、アセトンを用いて混合し、次に、キャスト法により、この混合物を厚さ10 μ mのアルミニウム箔上に塗布した。更に、これを100℃の温度で乾燥させた。これにより、正極集電体（アルミニウム箔）上に厚さが約100 μ mのシート状の正極を作製した。

【0029】負極の作製

負極の作製には、負極材料として市販の10 μ mの黒鉛粉末、結着剤としてフッ素樹脂（ポリビニリデンフルオライド（PVDF））を用いた。質量比で92:8の黒鉛粉末とポリビニリデンフルオライドを、アセトンを用いて混合し、次に、キャスト法により、この混合物を厚さ10 μ mの銅箔上に塗布した。更に、これを100℃の温度で乾燥させた。これにより、負極集電体（銅箔）上に厚さが約100 μ mのシート状の負極を作製した。

【0030】媒体の作製

実施例1と同様にシート状のガラスセラミックス複合媒体を作製した。

【0031】非水系電解液の調製

実施例1と同様に非水系電解液を調製した。

【0032】リチウム二次電池の組み立て

上記の正極、負極の間にセパレータとして上記のシート状ガラスセラミックス複合媒体を挟み込んで、ダブルローラーミニータによって接合し、正極集電体、正極、ガラスセラミックス複合媒体、負極、負極集電体の5層構造体を組み立てた。この5層構造体を、室温で上記非水系電解液に10分間浸漬して、ガラスセラミックス複合媒体に非水系電解液を含浸させて複合電解質とし、セパレータとしてこの複合電解質を備えたリチウム二次電池を作製した。非水系電解液の含浸量は複合電解質の質量の約60%であった。このリチウム二次電池の構造を図1に示す。図1のリチウム二次電池において、1は正極集電体、2は正極、3はガラスセラミックス複合電解質、4は負極、5は負極集電体を示す。1層が8cm²のこのリチウム二次電池をさらに6層積層させて、400mAh級のリチウム二次電池を組み立て、室温25℃において定電流で充放電サイクル試験を行った。この試験では、充電終了電圧4.2V、放電終了電圧3.0V、充電速度10mA/gm²とし、電池の放電容量を測定した。なお、このリチウム二次電池のエネルギー容量は1480mWhであった。

【0033】（比較例2）媒体の作製時に、リチウムイオン伝導性ガラスセラミックス粉末の替わりに、表面修飾された粉末状のフェウムドシリカ（SiO₂）を同量加入したこと以外は、実施例2と同様にリチウム二次電池を作製し、同条件にて充放電サイクル試験を行い、電池の放電容量を測定した。

【0034】実施例2及び比較例2で得られた電池それぞれの初期放電容量と300サイクル目の放電容量の測定結果を表1に示した。

【0035】

【表1】

	放電容量 [mAh/cm ²]	
	初期	300サイクル目
実施例2	7.1	6.4
比較例2	5.8	5.2

【0036】表1から明らかなように、本実施例2の電池は、比較例2に比べて放電容量が大きいことが分かる。また、この電池における理論電池容量は約8mAh/cm²であり、実施例2の電池では非常に近い値を示しており、優れたセル性能を有していることも分かる。

【0037】また、実施例2及び比較例2で得られた電池それぞれの充放電サイクルに伴う放電容量の変化を図2に示した。

【0038】図2より、初期においても、300サイクル目においても、実施例2の放電容量は比較例2の初期容量と比較してはるかに大きいことが明らかである。つまり、このリチウムイオン伝導性ガラスセラミックスを電解質に含有することによって、高容量なリチウム二次電池の作製が可能となった。

【0039】（実施例3）実施例2と同様に複合電解質を備えたリチウム二次電池を組み立て、同じく室温25℃において充電終了電圧4.2V、放電終了電圧3.0Vの条件下の充放電サイクル試験を実施例2に比較して3倍の急速充電を適用して行った。

【0040】（比較例3）比較例2と同様にリチウム二次電池を組み立て、同じく室温25℃において充電終了電圧4.2V、放電終了電圧3.0Vの同じ条件下の充放電サイクル試験を実施例2に比較して3倍の急速充電を適用して行った。

【0041】実施例3及び比較例3で得られた電池それぞれの初期放電容量と300サイクル目の放電容量の測定結果を表2に示した。

【0042】

【表2】

	放電容量 [mAh/cm ²]	
	初期	300サイクル目
実施例3	7.1	5.5
比較例4	5.4	4.3

【0043】表2から明らかなように、本実施例3の電池は、比較例3に比べて放電容量が大きいことが分かり、急速充電においても優れたセル性能を有していることも分かる。

【0044】また、実施例3及び比較例3で得られた電池それぞれの充放電サイクルに伴う放電容量の変化を図3に示した。

【0045】図3より、初期においても、300サイクル目においても、実施例3の放電容量は比較例3の初期容量と比較してはるかに大きいことが明らかである。

【0046】（実施例4）実施例2と同様に複合電解質を備えたリチウム二次電池を組み立て、充電終了電圧4

2V、放電終止電圧3.0Vの同じ条件下の充放電サイクル試験において作動温度を変化させて行った。試験は、-10℃、0℃、25℃、50℃、75℃の各温度で行った。

【0047】（比較例4）比較例2と同様にリチウム二次電池を組み立て、充電終止電圧4.2V、放電終止電圧3.0Vの同じ条件下の充放電サイクル試験において作動温度を変化させて行った。試験は、-10℃、0℃、25℃、50℃、75℃の各温度で行った。

【0048】実施例4及び比較例4で得られた電池それぞれその作動温度に対する初期放電容量の値の変化を図4に示した。

【0049】図4より、実施例4の電池は、-10℃から75℃まで広い温度範囲で大きな放電容量を維持し、比較例4と比較してもはるかに優れていることが明らかである。

【0050】（実施例5）媒体の作製時に、可塑剤として用いていたヘキサフルオロプロピレンHFPを使用せずに、ポリビニリデンフルオライド（PVDF）とリチウムイオン伝導性ガラスセラミックスのそれぞれの粉体を60:40の質量比で同様にアセトン懸濁液とし、シート状ガラスセラミックス複合媒体を作製したこと以外は、実施例2と同様に複合電解質を備えたリチウム二次電池を作製した。非水系電解液の含浸量は複合電解質の質量の約18%であった。

【0051】（比較例5）媒体の作製時に、リチウムイオン伝導性ガラスセラミックス粉体の替わりに、表面修飾された粉末状のフェウムドシリカ（SiO₂）を同量加えたこと以外は、実施例5と同様に電池を作製した。

【0052】可塑剤として使用していたヘキサフルオロプロピレン（HFP）を使用していない実施例5及び比較例4の電池では、どちらの場合も電解液の含浸性が遅く、ヘキサフルオロプロピレン（HFP）を使用した実施例4及び比較例4の電池と比較して3割程度の含浸率しかなかった。

【0053】実施例5及び比較例5で得られた電池それぞれその作動温度に対する初期放電容量の値の変化を図5に示した。

【0054】比較例2～4と比較して電解液を3割程度しか含まない比較例5の電池では、非常に小さい放電容量しか示さなかった。それに比べて同様に電解液を3割程度しか含まない実施例5の電池では、十分に高い放電容量を示し、比較例4とほぼ同等かそれ以上の容量が得られた。これは、複合電解質に含有させたリチウムイオン伝導性ガラスセラミックスの優位性によるものであ

る。つまり、リチウム二次電池内の有機液体成分である電解液の割合を減らした場合においても、十分に高い放電容量を有した電池の製造が可能であり、この結果さらに安全性に優れたリチウム二次電池が製造できることを示唆している。

【0055】

【発明の効果】以上記述したように、本発明における複合電解質を用いたリチウム二次電池用においては、複合電解質中にリチウムイオン伝導性ガラスセラミックス粉体を含有させるようにしたため、この複合電解質におけるリチウムイオンの伝導性が低下するということがなく、複合電解質における機械的強度が向上した上に、優れた電池容量を有するリチウム二次電池が得られるようになった。

【0056】また、上記のリチウムイオン伝導性ガラスセラミックスは充放電時に高分子材料からなる媒体と対応するということが少ないため、リチウム二次電池における放電容量が大きく、急激に低下することも抑制された優れたリチウム二次電池が得られるようになった。

【0057】さらに、安全性を高めるために有機電解液成分を減らした場合においても、高い放電容量を有したリチウム二次電池の製造が可能となった。

【図面の簡単な説明】

【図1】実施例2におけるガラスセラミックス複合電解質を備えたリチウム二次電池の内部構造を示した断面説明図である。

【図2】実施例2及び比較例2で得られた電池それぞれの充放電サイクルに伴う放電容量の変化を示すグラフである。

【図3】実施例3及び比較例3で得られた電池それぞれの充放電サイクルに伴う放電容量の変化を示すグラフである。

【図4】実施例4及び比較例4で得られた電池それぞれの温度条件に対する初期放電容量を示すグラフである。

【図5】実施例5及び比較例5で得られた電池それぞれの温度条件に対する初期放電容量を示すグラフである。

【符号の説明】

1：正極集電体

2：正極

3：ガラスセラミックス複合電解質

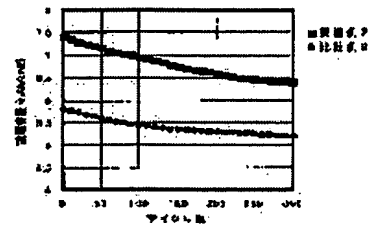
4：負極

5：負極集電体

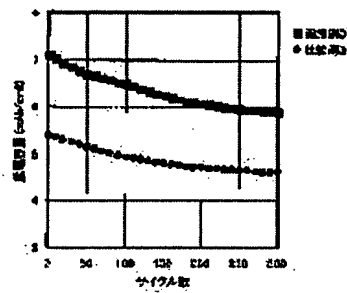
【図 1】



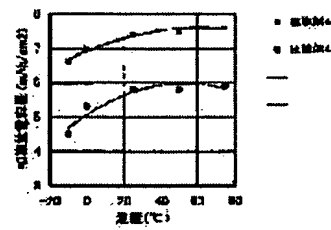
【図 2】



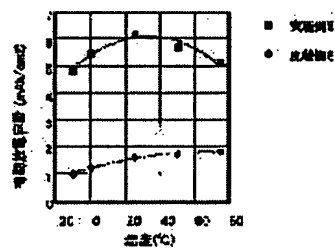
【図 3】



【図 4】



【図 5】



フロントページの続き

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(30)Priority

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(54) GLASS-CERAMIC COMPOSITE ELECTROLYTE AND LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide electrolyte having high ionic conductivity and sufficient mechanical strength even having thin thickness by impregnating a nonaqueous electrolytic solution in a medium including glass-ceramic powder of lithium ion conductivity.

SOLUTION: Preferably, this composite electrolyte is so formed that a glass ceramic body has a means grain size 20 μm or less (volume fraction) and the maximum grain size 44 μm or less, and composed of particles of lithium ion conductivity $1 \times 10^{-4} \text{ S.cm}^{-1}$ or more, a medium is formed by containing glass ceramic powder in a sheet polymer material, has the thickness 100 μm or less, and has the ionic conductivity $1 \times 10^{-5} \text{ S.cm}^{-1}$ or more, and the content of the glass-ceramic powder bodies in the medium is 10-90 wt.%. This lithium secondary battery comprises a positive electrode current collecting element 1, a positive electrode 2, glass-ceramic composite electrolyte 3, a negative electrode 4, and a negative electrode current collecting element 5. The composite electrolyte has lithium ion conductive glass-ceramic powder bodies therein so as to provide a secondary battery with superior battery capacity.



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CLAIMS

- [Claim(s)]
- [Claim 1]A crystallized glass compound electrolyte with which a nonaqueous electrolyte is impregnated into a medium containing a lithium ion conductivity crystallized glass granular material.
- [Claim 2]The compound electrolyte according to claim 1 in which mean particle diameter of 20 micrometers or less (volume fraction) and a maximum droplet size are 44 micrometers or less, and this crystallized glass granular material consists of particles more than lithium ion conductivity $1 \times 10^{-4} \text{S-cm}^{-1}$.
- [Claim 3]The compound electrolyte according to claim 1 or 2 in which this medium contains a crystallized glass granular material in a sheet-shaped polymer material.
- [Claim 4]It is a compound electrolyte given in any 1 paragraph among claims 1-3 which are 100 micrometers or less in thickness, and are more than ionic conductivity $1 \times 10^{-5} \text{S-cm}^{-1}$.
- [Claim 5]Content of a crystallized glass granular material in this medium is a compound electrolyte given in any 1 paragraph among claims 1-4 which are ten to 90 mass %.
- [Claim 6]A lithium secondary battery with which it is an anode, a negative electrode, and the lithium secondary battery provided with a separator, and this separator consists of a compound electrolyte given in any 1 paragraph among claims 1-5.
-

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the compound electrolyte containing a lithium ion conductivity crystallized glass granular material. This invention relates to the lithium secondary battery provided with this compound electrolyte.

[0002]

[Description of the Prior Art]Although the electrolysis solution of the drainage system or the non-drainage system was generally used as an electrolyte in a cell from the former, such a fluid replaces a central electrolyte in recent years, and the lithium secondary battery using the polymer electrolyte which comprised polymers came to attract attention.

[0003]That is, in this way, in the lithium secondary battery using a polymer electrolyte, since the electrolysis solution of a fluid was held in a polymer electrolyte, it was hard to spill liquid, and there was also little corrosiveness, it was simple for the structure of a cell, and had an advantage, like the assembly also becomes easy.

[0004]Here, since such a polymer electrolyte has the low conductivity of a lithium ion only compared with an electrolysis solution, making thickness of this polymer electrolyte thin came to be performed. However, when a polymer electrolyte was made thin in this way, that mechanical strength became low, this polymer electrolyte was destroyed at the time of production of a cell, and there was a problem of being easy to short-circuit an anode and a negative electrode.

[0005]Then, in the former, as shown in JP,6-140052,A etc., inorganic oxides, such as alumina, were added in the electrolyte, it was considered as the compound electrolyte, and raising a mechanical strength was proposed. Inorganic oxides, such as silica and ulmin acid lithium, are proposed besides alumina. However, when inorganic oxides, such as alumina, are made to add in an electrolyte, there is a problem to which the conductivity of the lithium ion in a compound electrolyte falls greatly. If it carries out by repeating charge and discharge in the lithium secondary battery provided with this compound electrolyte, an electrolyte and the above-mentioned inorganic oxide will be reacted and the charge-discharge cycle characteristic in a lithium secondary battery will fall greatly.

[0006]

[Problem(s) to be Solved by the Invention]In the electrolyte with which a nonaqueous electrolyte is impregnated into a medium, an object of this invention is to provide the electrolyte which has sufficient mechanical strength when it has high ion conductivity and thickness is made thin. In the lithium secondary battery provided with the electrolyte with which a nonaqueous electrolyte is impregnated as a separator, cell capacity of this invention is high, a charge-discharge cycle characteristic's is good, and sets it as another purpose to provide the lithium secondary battery which can use being stabilized in the long run.

[0007]

[Means for Solving the Problem]A result of this invention persons having added various packing in an electrolyte, and having conducted a detailed experiment, A crystallized glass compound electrolyte which made a crystallized glass granular material of a specific presentation distribute and contain in a polymer medium with a nonaqueous electrolyte found out that the conductivity of a remarkable high lithium ion was shown compared with a compound electrolyte having contained an inorganic oxide in which the conductivity of the conventional lithium ion is not shown. If a compound electrolyte obtained here is applied to a lithium secondary battery, Compared with a case where a compound electrolyte having contained an inorganic oxide in which the conventional lithium ion conductivity is not shown is applied to a lithium secondary battery, cell capacity is high, and it discovers that a

charge-discharge cycle characteristic also improves remarkably, and came to make this invention.

[0008] Namely, the invention of this application according to claim 1 is a crystallized glass compound electrolyte with which a nonaqueous electrolyte is impregnated into a medium containing a lithium ion conductivity crystallized glass granular material. The invention according to claim 2 this crystallized glass granular material Mean particle diameter of 20 micrometers or less (volume fraction), And a maximum droplet size is 44 micrometers or less, and it is the compound electrolyte according to claim 1 which consists of particles more than lithium ion conductivity $1 \times 10^{-4} \text{S} \cdot \text{cm}^{-1}$. To a sheet-shaped polymer material, the invention according to claim 3 is a crystallized glass granular material the compound electrolyte according to claim 1 or 2 to contain, and this medium the invention according to claim 4, It is a compound electrolyte given in any 1 paragraph among claims 1-3 which are 100 micrometers or less in thickness, and are more than ionic conductivity $1 \times 10^{-5} \text{S} \cdot \text{cm}^{-1}$. The invention according to claim 5 is a compound electrolyte given in any 1 paragraph among claims 1-4 whose content of a crystallized glass granular material in this medium is ten to 90 mass %, and the inventions according to claim 6 are an anode, a negative electrode, and the lithium secondary battery provided with a separator. This separator is a lithium secondary battery which consists of a compound electrolyte given in any 1 paragraph among claims 1-5.

[0009] And when a compound electrolyte of this invention makes a lithium ion conductivity crystallized glass granular material contain in a lithium ion conductivity electrolyte, It is rare for the conductivity of a lithium ion in an electrolyte to fall, an electrolytic mechanical strength improves, and cell capacity, especially charging capacity can also be further made high.

[0010] Since the above-mentioned crystallized glass granular material has low reactivity, it decreases that an electrolysis solution and this crystallized glass react at the time of charge and discharge, It also decreases that an electrolyte reacts like an electrolyte which added inorganic oxides, such as conventional alumina, and the charge-discharge cycle characteristic of a lithium secondary battery falls.

[0011] Since an electrode area per unit volume of a cell is large and the thinner one can secure a compound electrolyte of this invention when it is used as a cell, a cell of high capacity is obtained. Then, a compound electrolyte of this invention has [a sheet shaped of 100 micrometers or less] preferred thickness. As for a crystallized glass granular material, in a compound electrolyte of this invention, distributing uniformly in a medium is preferred in respect of the ion conductivity of a compound electrolyte, and a mechanical strength. In order to make dispersibility good, as for particle diameter of a crystallized glass granular material, 20 micrometers or less are [on an average] preferred, and its 10 micrometers or less are more preferred. As a maximum droplet size, 44 micrometers or less are preferred.

[0012] Since the mobility of a lithium ion at the time of charge and discharge of a rechargeable lithium-ion battery depends on electrolytic lithium ion conductivity, the higher one of lithium ion conductivity of a compound electrolyte of this invention is preferred. It is specifically preferred that it is more than $1 \times 10^{-5} \text{S} \cdot \text{cm}^{-1}$, and it is more preferred that it is more than $1 \times 10^{-4} \text{S} \cdot \text{cm}^{-1}$. More generally than lithium ion conductivity of the electrolysis solution itself, ionic conductivity of a gel solid electrolyte is low. As for electrolytic ion conductivity, falling further is common, if the lithium ion conductivity of add-in material itself is low when adding an inorganic oxide, since a mechanical strength is increased to a gel solid electrolyte. However, if a lithium ion conductivity crystallized glass granular material is used as add-in material, it is effective in preventing a fall of electrolytic lithium ion conductivity, and a compound electrolyte which has high ionic conductivity and sufficient mechanical strength after all can be obtained. As for a crystallized glass granular material as add-in material, in a compound electrolyte of this invention, it is desirable to consist of crystallized glass particles of lithium ion conductivity higher than lithium ion conductivity of a compound electrolyte. Lithium ion conductivity of crystallized glass particles which constitute a crystallized glass granular material is more than $1 \times 10^{-4} \text{S} \cdot \text{cm}^{-1}$ preferably, and, specifically, is more than $1 \times 10^{-3} \text{S} \cdot \text{cm}^{-1}$ more preferably.

[0013] Its things are [having flexibility and containing a crystallized glass granular material in various shape from a point which can be fabricated at a sheet-shaped polymer material] preferred while the medium which constitutes a compound electrolyte of this invention can enlarge cell capacity per volume when it uses as a cell. As for a medium which constitutes a compound electrolyte of this invention, it is preferred that it is a porous body which has a detailed hole so that a nonaqueous electrolyte may be impregnated and it may become gelatinous material.

[0014] As a sheet-shaped polymer material which constitutes a compound electrolyte of this invention, Polymer materials, such as fluoro-resins, such as polyolefines, such as polyethylene and polypropylene, polytetrafluoroethylene, polychlorotrifluoroethylene resin, and polyvinylidene fluoride, polyamide, and polyester

polyacrylate, can be used. It is required that it can be stabilized and can impregnate with an electrolysis solution as a material of a medium, that processability is good, that it excels in flexibility, that high ion conductivity with sufficient affinity with crystallized glass should be shown, etc. As what was provided with these character with sufficient balance, especially a fluoro-resin is preferred.

[0015] As a solute which constitutes a nonaqueous electrolyte in a compound electrolyte of this invention, For example, lithium hexafluorophosphate (LiPF_6), lithium tetrafluoroborate (LiBF_4), Lithium perchlorate (LiClO_4), hexa full OROHI acid lithium (LiAsF_6), Lithium compounds, such as lithium trifluoromethanesulfonate ($\text{LiCF}_3\text{SO}_3\text{LiClO}_4$) and trifluoro methanesulfon acid imide lithium ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$), can be used. As a solvent of the above-mentioned solute, for example Ethylene carbonate, Organic solvents, such as propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, gamma-butyrolactone, sulfolane, 1,2-dimethoxyethane, wood ether, and acetonitrile, can be used. The above-mentioned solute can be dissolved in the above-mentioned solvent, and it can be considered as a nonaqueous electrolyte, and can be used for a compound electrolyte of this invention. As for a compound electrolyte of this invention, it is preferred that it is gel. By making a compound electrolyte into gel, high concentration can be stabilized and impregnated with a nonaqueous electrolyte, and high ion conductivity can be revealed. A compound electrolyte of this invention can be made into gel by using these nonaqueous electrolytes.

[0016] Here, if there is little the quantity when making a lithium ion conductivity crystallized glass granular material which has high ionic conductivity in an electrolyte as mentioned above contain, improvement in lithium ion conductivity of a compound electrolyte is not found, and intensity in a compound electrolyte cannot fully be raised. Since content of an electrolysis solution will decrease on the other hand if the quantity increases too much, Since contact with a compound electrolyte and the above-mentioned crystallized glass granular material, and an electrode almost becomes solids, contact nature worsens and the mobility of a lithium ion between an electrode, a compound electrolyte, and the above-mentioned crystallized glass granular material worsens. Then, in a compound electrolyte of this invention, as a minimum of content of a lithium-ion-conductivity crystallized glass granular material in a medium, more than 10 mass % is preferred, and more than 20 mass % is more preferred. As a maximum, below 90 mass % is preferred, and below 80 mass % is more preferred.

[0017] A compound electrolyte of this invention contains a lithium ion conductivity crystallized glass granular material. As for this crystallized glass granular material, it is preferred that a main crystal phase consists of crystallized glass of $\text{Li}_{1+x}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$). This crystallized glass granular material heat-treats mother glass of a presentation of a $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{SiO}_2-\text{P}_2\text{O}_5$ system, It can obtain by making it crystallize as $\text{Li}_{1+x}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$, and grinding a main crystal phase after that. As a parameter of main crystal phase $\text{Li}_{1+x}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$, it is $0 \leq x \leq 1$ and $0 \leq y \leq 1$, and is $0 \leq x \leq 0.4$ and $0 < y \leq 0.6$ more preferably. As composition ratio of oxide conversion of mother glass, it is a mol% display and, as for Li_2O , it is [aluminum₂O₃ / TiO₂] preferred [5 to 10% / 35 to 45% / SiO₂ / 1 to 10% / P₂O₅] 12 to 18% that it is 30 to 40%. In the case of this composition range, the cast of the melting glass can be carried out, glass can be obtained easily, and crystallized glass with the above-mentioned crystal phase produced by heat-treating this mother glass has high lithium ion conductivity.

[0018] A lithium secondary battery of this invention is provided with a crystallized glass compound electrolyte as an anode, a negative electrode, and a separator. In a lithium secondary battery of this invention, occlusion of lithium and a transition metal compound which can be emitted can be used as the main ingredients as a material used for the anode. For example, a transition metal oxide containing a transition metal and lithium, such as manganese, cobalt, nickel, vanadium, niobium, molybdenum, and titanium, can be used as the main ingredients. An anode which contains cobalt acid lithium as the main ingredients especially is excellent in respect of higher electromotive force and a cycle characteristic.

[0019] In a lithium secondary battery of this invention, occlusion of metal lithium or lithium, an alloy which can be emitted, an oxide, a carbon material, etc. can be used as a material used for the negative electrode.

[0020]

[Embodiment of the Invention] A concrete example is hereafter given and described about the compound electrolyte concerning this invention, and the lithium secondary battery provided with this, and the point that the compound electrolyte which gives a comparative example and is built over this invention, and the lithium secondary battery provided with this are excellent is clarified. This invention is not limited to what was shown in

the following example, in the range which does not change the gist, is changed suitably and can be carried out.
[0021](Example 1)

As a production raw material of a lithium-ion-conductivity crystallized glass granular material, $\text{NH}_4\text{H}_2\text{PO}_4$, aluminum(PO_3)₃, Li_2CO_3 , SiO_2 , Use TiO_2 and for these P_2O_5 by mol% of oxide conversion 35.0%, For aluminum₂O₃ 7.5% 15.0%, After carrying out weighing and mixing uniformly so that it may become the presentation to which TiO_2 was said 38.0% and to which SiO_2 was said as 4.5%, it put into the platinum pot, and the heating dissolution was carried out for 2 hours, agitating glass melt at 1500 ** among an electric furnace. Then, the cast of the glass melt was carried out underwater directly, and mother glass was obtained. Target crystallized glass was obtained by performing heat treatment of 12 hours for this mother glass at 950 **. As for the crystal phase which deposited, it was checked by powder X-ray diffractometry that $\text{Li}_{1+x+y}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($0 \leq x \leq 0.4$, $0 < y \leq 0.6$) is a main crystal phase. The ionic conductivity of the crystallized glass was $1.4 \times 10^{-3} \text{S}\cdot\text{cm}^{-1}$ in the room temperature of 25 **. After grinding this crystallized glass using a planetary ball mill, the classification was performed, and the lithium-ion-conductivity crystallized glass granular material with a mean particle diameter of 7 micrometers was obtained.

[0022]The 20 mass % injection of each granular material of the production polyvinylidene fluoride (PVdF) of a medium, hexafluoropropylene (HFP), and the above-mentioned lithium-ion-conductivity crystallized glass was done with the mass ratio of 35:40:25 at acetone, and acetone suspension was prepared. After forming this liquid with casting method, vacuum drying was carried out and the 50-micrometer-thick sheet-shaped crystallized glass composite medium was produced.

[0023]Lithium hexafluorophosphate (LiPF_6) was dissolved in the solvent which mixed preparation ethylene carbonate (EC) and dimethyl carbonate (DMC) of the nonaqueous electrolyte with the mass ratio of 50:50 by the concentration of 1 mol/L, and it was considered as the nonaqueous electrolyte.

[0024]The sheet shaped compound electrolyte which consists of gelatinous material was obtained by immersing the production above-mentioned crystallized glass composite medium of a compound electrolyte in the above-mentioned nonaqueous electrolyte for 10 minutes at a room temperature.

[0025]The compound electrolyte in which ***** of ionic conductivity was obtained was inserted with the stainless steel sheet of two sheets, and the sample for lithium ion conductometry was produced by using these stainless steel sheets as an electrode. As a result of performing impedance measurement in a room temperature and asking for ionic conductivity, ionic conductivity was $3.1 \times 10^{-4} \text{S}\cdot\text{cm}^{-1}$.

[0026](Comparative example 1) At the time of production of a medium, except having added an equivalent amount of fumed silica (SiO_2) by which surface ornamentation was carried out instead of lithium-ion-conductivity crystallized glass, the sheet-shaped compound electrolyte was produced like Example 1, and it asked for ionic conductivity in a similar manner. As a result, ionic conductivity was $1.7 \times 10^{-4} \text{S}\cdot\text{cm}^{-1}$. When Example 1 was compared with the comparative example 1, the ionic conductivity of each compound electrolyte film brought a result with the higher double [about] example 1. This is an effect containing ion-conductive crystallized glass.

[0027]The example of production of (Example 2) next an anode, a negative electrode, and the lithium secondary battery provided with the crystallized glass compound electrolyte as a separator is explained.

[0028]Acetylene black was used for production of the production anodes of an anode as commercial cobalt acid lithium (LiCoO_2) and a conducting agent as a positive electrode material, and fluororesin powder (polyvinylidene fluoride (PVdF)) was used for it as a binder. With the mass ratio, cobalt acid lithium of 82:10:8, acetylene black, and polyvinylidene fluoride were mixed using acetone, next this mixture was applied on 10-micrometer-thick aluminium foil with casting method. This was dried at the temperature of 100 **. This produced the sheet shaped anode about 100 micrometers thick on the positive pole collector (aluminium foil).

[0029]The fluoro-resin (polyvinylidene fluoride (PVdF)) was used for production of the production negative electrodes of a negative electrode as 10-micrometer commercial graphite powder and a binder as a negative pole material. With the mass ratio, polyvinylidene fluoride was mixed with the graphite powder of 92:8 using acetone, next this mixture was applied on 10-micrometer-thick copper foil with casting method. This was dried at the temperature of 100 **. This produced the sheet shaped negative electrode about 100 micrometers thick on the negative pole collector (copper foil).

[0030]The sheet shaped crystallized glass composite medium was produced like the production examples 1 of a

medium.

[0031]The nonaqueous electrolyte was prepared like the preparation examples 1 of a nonaqueous electrolyte.

[0032]The above-mentioned sheet-shaped crystallized glass composite medium was put as a separator between the anode of the assembly above of a lithium secondary battery, and the negative electrode, it pasted up with the double roller laminator, and 5 layered structure of a positive pole collector, an anode, the crystallized glass composite medium, the negative electrode, and the negative pole collector was assembled. This 5 layered structure was immersed in the above-mentioned nonaqueous electrolyte for 10 minutes at the room temperature, and the crystallized glass composite medium was impregnated with the nonaqueous electrolyte, it was considered as the compound electrolyte, and the lithium secondary battery provided with this compound electrolyte as a separator was produced. The amount of being impregnated of the nonaqueous electrolyte was about 60% of the mass of the compound electrolyte. The structure of this lithium secondary battery is shown in drawing 1. In the lithium secondary battery of drawing 1, an anode and 3 show a crystallized glass compound electrolyte, 4 shows a negative electrode, and, as for a positive pole collector and 2, 1 shows a negative pole collector 5. One layer made six more layers of this lithium secondary battery of 8 cm² laminate, finished setting up a 400mAh class lithium secondary battery, and did the charge-and-discharge cycle test by constant current in the room temperature of 25 **. In this examination, it was considered as the charge final voltage 4.2V, the discharge final voltage 3.0V, and charge speed 10 mA/cm², and the service capacity of the cell was measured. The energy capacity of this lithium secondary battery was 1480mWh.

[0033](Comparative example 2) At the time of production of a medium, instead of a lithium-ion-conductivity crystallized glass granular material, Except having added an equivalent amount of powdered fumed silica (SiO₂) by which surface ornamentation was carried out, the lithium secondary battery was produced like Example 2, the charge-and-discharge cycle test was done on the conditions, and the service capacity of the cell was measured.

[0034]The measurement result of the initial service capacity of each cell and the service capacity of a 300 cycle eye obtained by Example 2 and the comparative example 2 was shown in Table 1.

[0035]

[Table 1]

	放電容量 (mAh/cm ²)	
	初期	300サイクル目
実施例 2	7.4	6.4
比較例 2	5.8	5.2

[0036]The cell of this example 2 is understood that service capacity is large compared with the comparative example 2 so that clearly from Table 1. The theoretical cell capacity in this cell is about 8 mAh/cm², and by the cell of Example 2, the very near value is shown and it also turns out that it has the outstanding cell performance.

[0037]Change of the service capacity accompanying the charging and discharging cycle of each cell obtained by Example 2 and the comparative example 2 was shown in drawing 2.

[0038]Also in the first stage, the far large thing of service capacity of Example 2 is clearer also in a 300 cycle eye than in drawing 2 as compared with the initial capacity of the comparative example 2. That is, it became producible [a high capacity lithium secondary battery] by containing this lithium-ion-conductivity crystallized glass in an electrolyte.

[0039](Example 3) The lithium secondary battery provided with the compound electrolyte like Example 2 was assembled, and, similarly the charge-and-discharge cycle test under the conditions of the charge final voltage 4.2V and the discharge final voltage 3.0V was done with the application of 3 times as much boost charge in the room temperature of 25 ** as compared with Example 2.

[0040](Comparative example 3) The lithium secondary battery was assembled like the comparative example 2, and, similarly the charge-and-discharge cycle test under the same conditions of the charge final voltage 4.2V and the discharge final voltage 3.0V was done with the application of 3 times as much boost charge in the room temperature of 25 ** as compared with Example 2.

[0041]The measurement result of the initial service capacity of each cell and the service capacity of a 300 cycle eye obtained by Example 3 and the comparative example 3 was shown in Table 2.

[0042]

[Table 2]

	放電容量 (mAh/cm ²)	
	初期	300サイクル目
実施例 3	7.1	5.9
比較例 4	5.4	4.6

[0043]The cell of this example 3 is understood that service capacity is large compared with the comparative example 3, and it also turns out that it has the cell performance outstanding also in boost charge so that clearly from Table 2.

[0044]Change of the service capacity accompanying the charging and discharging cycle of each cell obtained by Example 3 and the comparative example 3 was shown in drawing 3.

[0045]Also in the first stage, the far large thing of service capacity of Example 3 is clearer also in a 300 cycle eye than in drawing 3 as compared with the initial capacity of the comparative example 3.

[0046](Example 4) The lithium secondary battery provided with the compound electrolyte like Example 2 was assembled, and it carried out by changing operating temperature in the charge-and-discharge cycle test under the same conditions of the charge final voltage 4.2V and the discharge final voltage 3.0V. The examination was done at each temperature of -10 **, 0 **, 25 **, 50 **, and 75 **.

[0047](Comparative example 4) The lithium secondary battery was assembled like the comparative example 2, and it carried out by changing operating temperature in the charge-and-discharge cycle test under the same conditions of the charge final voltage 4.2V and the discharge final voltage 3.0V. The examination was done at each temperature of -10 **, 0 **, 25 **, 50 **, and 75 **.

[0048]Change of the value of the initial service capacity to the operating temperature of each cell obtained by Example 4 and the comparative example 4 was shown in drawing 4.

[0049]Even if the cell of Example 4 maintains big service capacity in -10 ** to 75 **, and a wide temperature requirement and measures it with the comparative example 4, its excelling far is clearer than drawing 4.

[0050](Example 5), without using the used hexafluoropropylene HFP as a plasticizer at the time of production of a medium, Each granular material of polyvinylidene fluoride (PVdF) and lithium-ion-conductivity crystallized glass is similarly used as acetone suspension with the mass ratio of 60:40, The lithium secondary battery provided with the compound electrolyte like Example 2 was produced except having produced the sheet-shaped crystallized glass composite medium. The amount of being impregnated of the nonaqueous electrolyte was about 18% of the mass of the compound electrolyte.

[0051](Comparative example 5) At the time of production of a medium, the cell was produced like Example 5 except having added an equivalent amount of powdered fumed silica (SiO₂) by which surface ornamentation was carried out instead of the lithium-ion-conductivity crystallized glass granular material.

[0052]In the cell of Example 5 and the comparative example 4 which are not using the hexafluoropropylene (HFP) which was being used as a plasticizer. In both cases, the impregnating ability of the electrolysis solution was bad and had only the rate of impregnation of about 30 percent as compared with the cell of Example 4 and the comparative example 4 which use hexafluoropropylene (HFP).

[0053]Change of the value of the initial service capacity to the operating temperature of each cell obtained by Example 5 and the comparative example 5 was shown in drawing 5.

[0054]The cell of the comparative example 5 which contains an electrolysis solution only about 30 percent as compared with the comparative examples 2-4 showed only very small service capacity. In the cell of Example 5 which contains an electrolysis solution only about 30 percent in a similar manner compared with it, service capacity high enough was shown, it was almost equivalent to the comparative example 4, or the capacity beyond it was obtained. This is based on the predominance of the lithium-ion-conductivity crystallized glass which the compound electrolyte was made to contain. That is, also in the case where the rate of the electrolysis solution which is an organic liquid component in a lithium secondary battery is reduced, it has suggested that manufacture of a cell with service capacity high enough is possible, and the lithium secondary battery which was further excellent in safety as a result can be manufactured.

[0055]

[Effect of the Invention]In the object for lithium secondary batteries using a compound electrolyte [in / as described above / this invention], Having made it make a lithium-ion-conductivity crystallized glass granular material contain in a compound electrolyte A sake, There is nothing about the conductivity of the lithium ion in this compound electrolyte falling, and the lithium secondary battery which has the cell capacity whose mechanical

strength in a compound electrolyte improved and also which was excellent came to be obtained.
[0056]The outstanding lithium secondary battery with which the service capacity in a lithium secondary battery being large, and falling rapidly was also controlled since it was rare for the above-mentioned lithium-ion-conductivity crystallized glass to react to the medium which consists of polymer materials at the time of charge and discharge came to be obtained.
[0057]In order to improve safety, also in the case where an organic electrolysis liquid component is reduced, manufacture of the lithium secondary battery with high service capacity was attained.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the compound electrolyte containing a lithium ion conductivity crystallized glass granular material. This invention relates to the lithium secondary battery provided with this compound electrolyte.

[Translation done.]

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PRIOR ART

[Description of the Prior Art]Although the electrolysis solution of the drainage system or the non-drainage system was generally used as an electrolyte in a cell from the former, such a fluid replaces a central electrolyte in recent years, and the lithium secondary battery using the polymer electrolyte which comprised polymers came to attract attention.

[0003]That is, in this way, in the lithium secondary battery using a polymer electrolyte, since the electrolysis solution of a fluid was held in a polymer electrolyte, it was hard to spill liquid, and there was also little corrosiveness, it was simple for the structure of a cell, and had an advantage, like the assembly also becomes easy.

[0004]Here, since such a polymer electrolyte has the low conductivity of a lithium ion only compared with an electrolysis solution, making thickness of this polymer electrolyte thin came to be performed. However, when a polymer electrolyte was made thin in this way, that mechanical strength became low, this polymer electrolyte was destroyed at the time of production of a cell, and there was a problem of being easy to short-circuit an anode and a negative electrode.

[0005]Then, in the former, as shown in JP,6-140052,A etc., inorganic oxides, such as alumina, were added in the electrolyte, it was considered as the compound electrolyte, and raising a mechanical strength was proposed. Inorganic oxides, such as silica and ulmin acid lithium, are proposed besides alumina. However, when inorganic oxides, such as alumina, are made to add in an electrolyte, there is a problem to which the conductivity of the lithium ion in a compound electrolyte falls greatly. If it carries out by repeating charge and discharge in the lithium secondary battery provided with this compound electrolyte, an electrolyte and the above-mentioned inorganic oxide will be reacted and the charge-discharge cycle characteristic in a lithium secondary battery will fall greatly.

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EFFECT OF THE INVENTION

[Effect of the Invention]In the object for lithium secondary batteries using a compound electrolyte [in / as described above / this invention], Having made it make a lithium-ion-conductivity crystallized glass granular material contain in a compound electrolyte A sake, There is nothing about the conductivity of the lithium ion in this compound electrolyte falling, and the lithium secondary battery which has the cell capacity whose mechanical strength in a compound electrolyte improved and also which was excellent came to be obtained.

[0056]The outstanding lithium secondary battery with which the service capacity in a lithium secondary battery being large, and falling rapidly was also controlled since it was rare for the above-mentioned lithium-ion-conductivity crystallized glass to react to the medium which consists of polymer materials at the time of charge and discharge came to be obtained.

[0057]In order to improve safety, also in the case where an organic electrolysis liquid component is reduced, manufacture of the lithium secondary battery with high service capacity was attained.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]In the electrolyte with which a nonaqueous electrolyte is impregnated
nto a medium, an object of this invention is to provide the electrolyte which has sufficient mechanical strength
when it has high ion conductivity and thickness is made thin. In the lithium secondary battery provided with the
electrolyte with which a nonaqueous electrolyte is impregnated as a separator, cell capacity of this invention is
high, a charge-discharge cycle characteristic's is good, and sets it as another purpose to provide the lithium
secondary battery which can use being stabilized in the long run.

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MEANS

[Means for Solving the Problem]A result of this invention persons having added various packing in an electrolyte, and having conducted a detailed experiment, A crystallized glass compound electrolyte which made a crystallized glass granular material of a specific presentation distribute and contain in a polymer medium with a nonaqueous electrolyte found out that the conductivity of a remarkable high lithium ion was shown compared with a compound electrolyte having contained an inorganic oxide in which the conductivity of the conventional lithium ion is not shown. If a compound electrolyte obtained here is applied to a lithium secondary battery, Compared with a case where a compound electrolyte having contained an inorganic oxide in which the conventional lithium ion conductivity is not shown is applied to a lithium secondary battery, cell capacity is high, and it discovers that a charge-discharge cycle characteristic also improves remarkably, and came to make this invention.

[0008]Namely, the invention of this application according to claim 1 is a crystallized glass compound electrolyte with which a nonaqueous electrolyte is impregnated into a medium containing a lithium ion conductivity crystallized glass granular material, The invention according to claim 2 this crystallized glass granular material Mean particle diameter of 20 micrometers or less (volume fraction), And a maximum droplet size is 44 micrometers or less, and t is the compound electrolyte according to claim 1 which consists of particles more than lithium ion conductivity $1 \times 10^{-4} \text{S-cm}^{-1}$, To a sheet-shaped polymer material, the invention according to claim 3 is a crystallized glass granular material the compound electrolyte according to claim 1 or 2 to contain, and this medium the invention according to claim 4, It is a compound electrolyte given in any 1 paragraph among claims 1-3 which are 100 micrometers or less in thickness, and are more than ionic conductivity $1 \times 10^{-5} \text{S-cm}^{-1}$, The invention according to claim 5 is a compound electrolyte given in any 1 paragraph among claims 1-4 whose content of a crystallized glass granular material in this medium is ten to 90 mass %, and the inventions according to claim 6 are an anode, a negative electrode, and the lithium secondary battery provided with a separator, This separator is a lithium secondary battery which consists of a compound electrolyte given in any 1 paragraph among claims 1-5.

[0009]And when a compound electrolyte of this invention makes a lithium ion conductivity crystallized glass granular material contain in a lithium ion conductivity electrolyte, It is rare for the conductivity of a lithium ion in an electrolyte to fall, an electrolytic mechanical strength improves, and cell capacity, especially charging capacity can also be further made high.

[0010]Since the above-mentioned crystallized glass granular material has low reactivity, it decreases that an electrolysis solution and this crystallized glass react at the time of charge and discharge, It also decreases that an electrolyte reacts like an electrolyte which added inorganic oxides, such as conventional alumina, and the charge-discharge cycle characteristic of a lithium secondary battery falls.

[0011]Since an electrode area per unit volume of a cell is large and the thinner one can secure a compound electrolyte of this invention when it is used as a cell, a cell of high capacity is obtained. Then, a compound electrolyte of this invention has [a sheet shaped of 100 micrometers or less] preferred thickness. As for a crystallized glass granular material, in a compound electrolyte of this invention, distributing uniformly in a medium is preferred in respect of the ion conductivity of a compound electrolyte, and a mechanical strength. In order to make dispersibility good, as for particle diameter of a crystallized glass granular material, 20 micrometers or less are [on an average] preferred, and its 10 micrometers or less are more preferred. As a maximum droplet size, 44 micrometers or less are preferred.

[0012]Since the mobility of a lithium ion at the time of charge and discharge of a rechargeable lithium-ion battery depends on electrolytic lithium ion conductivity, the higher one of lithium ion conductivity of a compound electrolyte of this invention is preferred. It is specifically preferred that it is more than $1 \times 10^{-5} \text{S-cm}^{-1}$, and it is

more preferred that it is more than $1 \times 10^{-4} \text{S-cm}^{-1}$. More generally than lithium ion conductivity of the electrolysis solution itself, ionic conductivity of a gel solid electrolyte is low. As for electrolytic ion conductivity, falling further is common, if the lithium ion conductivity of add-in material itself is low when adding an inorganic oxide, since a mechanical strength is increased to a gel solid electrolyte. However, if a lithium ion conductivity crystallized glass granular material is used as add-in material, it is effective in preventing a fall of electrolytic lithium ion conductivity, and a compound electrolyte which has high ionic conductivity and sufficient mechanical strength after all can be obtained. As for a crystallized glass granular material as add-in material, in a compound electrolyte of this invention, it is desirable to consist of crystallized glass particles of lithium ion conductivity higher than lithium ion conductivity of a compound electrolyte. Lithium ion conductivity of crystallized glass particles which constitute a crystallized glass granular material is more than $1 \times 10^{-4} \text{S-cm}^{-1}$ preferably, and, specifically, is more than $1 \times 10^{-3} \text{S-cm}^{-1}$ more preferably.

[0013] Its things are [having flexibility and containing a crystallized glass granular material in various shape from a point which can be fabricated at a sheet-shaped polymer material] preferred while the medium which constitutes a compound electrolyte of this invention can enlarge cell capacity per volume when it uses as a cell. As for a medium which constitutes a compound electrolyte of this invention, it is preferred that it is a porous body which has a detailed hole so that a nonaqueous electrolyte may be impregnated and it may become gelatinous material.

[0014] As a sheet-shaped polymer material which constitutes a compound electrolyte of this invention, Polymer materials, such as fluoro-resins, such as polyolefines, such as polyethylene and polypropylene, polytetrafluoroethylene, polychlorotrifluoroethylene resin, and polyvinylidene fluoride, polyamide, and polyester polyacrylate, can be used. It is required that it can be stabilized and can impregnate with an electrolysis solution as a material of a medium, that processability is good, that it excels in flexibility, that high ion conductivity with sufficient affinity with crystallized glass should be shown, etc. As what was provided with these character with sufficient balance, especially a fluoro-resin is preferred.

[0015] As a solute which constitutes a nonaqueous electrolyte in a compound electrolyte of this invention, For example, lithium hexafluorophosphate (LiPF_6), lithium tetrafluoroborate (LiBF_4), Lithium perchlorate (LiClO_4), hexa full OROHI acid lithium (LiAsF_6), Lithium compounds, such as lithium trifluoromethanesulfonate ($\text{LiCF}_3\text{SO}_3\text{LiClO}_4$) and trifluoro methanesulfon acid imide lithium ($\text{Li}(\text{CF}_3\text{SO}_2)_2$), can be used. As a solvent of the above-mentioned solute, for example Ethylene carbonate, Organic solvents, such as propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, gamma-butyrolactone, sulfolane, 1,2-dimethoxyethane, wood ether, and acetonitrile, can be used. The above-mentioned solute can be dissolved in the above-mentioned solvent, and it can be considered as a nonaqueous electrolyte, and can be used for a compound electrolyte of this invention. As for a compound electrolyte of this invention, it is preferred that it is gel. By making a compound electrolyte into gel, high concentration can be stabilized and impregnated with a nonaqueous electrolyte, and high ion conductivity can be revealed. A compound electrolyte of this invention can be made into gel by using these nonaqueous electrolytes.

[0016] Here, if there is little the quantity when making a lithium ion conductivity crystallized glass granular material which has high ionic conductivity in an electrolyte as mentioned above contain, improvement in lithium ion conductivity of a compound electrolyte is not found, and intensity in a compound electrolyte cannot fully be raised. Since content of an electrolysis solution will decrease on the other hand if the quantity increases too much, Since contact with a compound electrolyte and the above-mentioned crystallized glass granular material, and an electrode almost becomes solids, contact nature worsens and the mobility of a lithium ion between an electrode, a compound electrolyte, and the above-mentioned crystallized glass granular material worsens. Then, in a compound electrolyte of this invention, as a minimum of content of a lithium-ion-conductivity crystallized glass granular material in a medium, more than 10 mass % is preferred, and more than 20 mass % is more preferred. As a maximum, below 90 mass % is preferred, and below 80 mass % is more preferred.

[0017] A compound electrolyte of this invention contains a lithium ion conductivity crystallized glass granular material. As for this crystallized glass granular material, it is preferred that a main crystal phase consists of crystallized glass of $\text{Li}_{1+x+y}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($0 < x \leq 1$, $0 < y \leq 1$). This crystallized glass granular material heat-treats mother glass of a presentation of a $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{SiO}_2-\text{P}_2\text{O}_5$ system, It can obtain by making it crystallize as $\text{Li}_{1+x+y}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$, and grinding a main crystal phase after that. As a parameter of main crystal phase $\text{Li}_{1+x+y}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$, it is $0 < x \leq 1$ and $0 < y \leq 1$, and is $0 < x \leq 0.4$ and $0 < y \leq 0.6$

more preferably. As composition ratio of oxide conversion of mother glass, it is a mol% display and, as for Li_2O , it is [aluminum $_2\text{O}_3$ / TiO_2] preferred [5 to 10% / 35 to 45% / SiO_2 / 1 to 10% / P_2O_5] 12 to 18% that it is 30 to 40%. In the case of this composition range, the cast of the melting glass can be carried out, glass can be obtained easily, and crystallized glass with the above-mentioned crystal phase produced by heat-treating this mother glass has high lithium ion conductivity.

[0018]A lithium secondary battery of this invention is provided with a crystallized glass compound electrolyte as an anode, a negative electrode, and a separator. In a lithium secondary battery of this invention, occlusion of lithium and a transition metal compound which can be emitted can be used as the main ingredients as a material used for the anode. For example, a transition metal oxide containing a transition metal and lithium, such as manganese, cobalt, nickel, vanadium, niobium, molybdenum, and titanium, can be used as the main ingredients. An anode which contains cobalt acid lithium as the main ingredients especially is excellent in respect of higher electromotive force and a cycle characteristic.

[0019]In a lithium secondary battery of this invention, occlusion of metal lithium or lithium, an alloy which can be emitted, an oxide, a carbon material, etc. can be used as a material used for the negative electrode.

[0020]

[Embodiment of the Invention]A concrete example is hereafter given and described about the compound electrolyte concerning this invention, and the lithium secondary battery provided with this, and the point that the compound electrolyte which gives a comparative example and is built over this invention, and the lithium secondary battery provided with this are excellent is clarified. This invention is not limited to what was shown in the following example, in the range which does not change the gist, is changed suitably and can be carried out.

[0021](Example 1)

As a production raw material of a lithium-ion-conductivity crystallized glass granular material, $\text{NH}_4\text{H}_2\text{PO}_4$, aluminum(PO_3) $_3$, Li_2CO_3 , SiO_2 , Use TiO_2 and for these P_2O_5 by mol% of oxide conversion 35.0%, For aluminum $_2\text{O}_3$ Li_2O 7.5% 15.0%, After carrying out weighing and mixing uniformly so that it may become the presentation to which TiO_2 was said 38.0% and to which SiO_2 was said as 4.5%, it put into the platinum pot, and the heating dissolution was carried out for 2 hours, agitating glass melt at 1500 ** among an electric furnace. Then, the cast of the glass melt was carried out underwater directly, and mother glass was obtained. Target crystallized glass was obtained by performing heat treatment of 12 hours for this mother glass at 950 **. As for the crystal phase which deposited, it was checked by powder X-ray diffractometry that $\text{Li}_{1+x+y}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($0 \leq x \leq 0.4$, $0 < y \leq 0.6$) is a main crystal phase. The ionic conductivity of the crystallized glass was $1.4 \times 10^{-3} \text{S-cm}^{-1}$ in the room temperature of 25 **. After grinding this crystallized glass using a planetary ball mill, the classification was performed, and the lithium-ion-conductivity crystallized glass granular material with a mean particle diameter of 7 micrometers was obtained.

[0022]The 20 mass % injection of each granular material of the production polyvinylidene fluoride (PVdF) of a medium, hexafluoropropylene (HFP), and the above-mentioned lithium-ion-conductivity crystallized glass was done with the mass ratio of 35:40:25 at acetone, and acetone suspension was prepared. After forming this liquid with casting method, vacuum drying was carried out and the 50-micrometer-thick sheet-shaped crystallized glass composite medium was produced.

[0023]Lithium hexafluorophosphate (LiPF_6) was dissolved in the solvent which mixed preparation ethylene carbonate (EC) and dimethyl carbonate (DMC) of the nonaqueous electrolyte with the mass ratio of 50:50 by the concentration of 1 mol/L, and it was considered as the nonaqueous electrolyte.

[0024]The sheet shaped compound electrolyte which consists of gelatinous material was obtained by immersing the production above-mentioned crystallized glass composite medium of a compound electrolyte in the above-mentioned nonaqueous electrolyte for 10 minutes at a room temperature.

[0025]The compound electrolyte in which ***** of ionic conductivity was obtained was inserted with the stainless steel sheet of two sheets, and the sample for lithium ion conductometry was produced by using these stainless steel sheets as an electrode. As a result of performing impedance measurement in a room temperature and asking for ionic conductivity, ionic conductivity was $3.1 \times 10^{-4} \text{S-cm}^{-1}$.

[0026](Comparative example 1) At the time of production of a medium, except having added an equivalent amount of fumed silica (SiO_2) by which surface ornamentation was carried out instead of lithium-ion-conductivity

crystallized glass, the sheet-shaped compound electrolyte was produced like Example 1, and it asked for ionic conductivity in a similar manner. As a result, ionic conductivity was $1.7 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$. When Example 1 was compared with the comparative example 1, the ionic conductivity of each compound electrolyte film brought a result with the higher double [about] example 1. This is an effect containing ion-conductive crystallized glass.

[0027]The example of production of (Example 2) next an anode, a negative electrode, and the lithium secondary battery provided with the crystallized glass compound electrolyte as a separator is explained.

[0028]Acetylene black was used for production of the production anodes of an anode as commercial cobalt acid lithium (LiCoO_2) and a conducting agent as a positive electrode material, and fluororesin powder (polyvinylidene fluoride (PVdF)) was used for it as a binder. With the mass ratio, cobalt acid lithium of 82:10:8, acetylene black, and polyvinylidene fluoride were mixed using acetone, next this mixture was applied on 10-micrometer-thick aluminium foil with casting method. This was dried at the temperature of 100 **. This produced the sheet shaped anode about 100 micrometers thick on the positive pole collector (aluminium foil).

[0029]The fluoro-resin (polyvinylidene fluoride (PVdF)) was used for production of the production negative electrodes of a negative electrode as 10-micrometer commercial graphite powder and a binder as a negative pole material. With the mass ratio, polyvinylidene fluoride was mixed with the graphite powder of 92:8 using acetone, next this mixture was applied on 10-micrometer-thick copper foil with casting method. This was dried at the temperature of 100 **. This produced the sheet shaped negative electrode about 100 micrometers thick on the negative pole collector (copper foil).

[0030]The sheet shaped crystallized glass composite medium was produced like the production examples 1 of a medium.

[0031]The nonaqueous electolyte was prepared like the preparation examples 1 of a nonaqueous electolyte.

[0032]The above-mentioned sheet-shaped crystallized glass composite medium was put as a separator between the anode of the assembly above of a lithium secondary battery, and the negative electrode, it pasted up with the double roller laminator, and 5 layered structure of a positive pole collector, an anode, the crystallized glass composite medium, the negative electrode, and the negative pole collector was assembled. This 5 layered structure was immersed in the above-mentioned nonaqueous electolyte for 10 minutes at the room temperature, and the crystallized glass composite medium was impregnated with the nonaqueous electolyte, it was considered as the compound electrolyte, and the lithium secondary battery provided with this compound electrolyte as a separator was produced. The amount of being impregnated of the nonaqueous electolyte was about 60% of the mass of the compound electrolyte. The structure of this lithium secondary battery is shown in drawing 1. In the lithium secondary battery of drawing 1, an anode and 3 show a crystallized glass compound electrolyte, 4 shows a negative electrode, and, as for a positive pole collector and 2, 1 shows a negative pole collector 5. One layer made six more layers of this lithium secondary battery of 8 cm^2 laminate, finished setting up a 400mAh class lithium secondary battery, and did the charge-and-discharge cycle test by constant current in the room temperature of 25 **. In this examination, it was considered as the charge final voltage 4.2V, the discharge final voltage 3.0V, and charge speed 10 mA/cm^2 , and the service capacity of the cell was measured. The energy capacity of this lithium secondary battery was 1480mWh.

[0033](Comparative example 2) At the time of production of a medium, instead of a lithium-ion-conductivity crystallized glass granular material, Except having added an equivalent amount of powdered fumed silica (SiO_2) by which surface ornamentation was carried out, the lithium secondary battery was produced like Example 2, the charge-and-discharge cycle test was done on the conditions, and the service capacity of the cell was measured.

[0034]The measurement result of the initial service capacity of each cell and the service capacity of a 300 cycle were obtained by Example 2 and the comparative example 2 was shown in Table 1.

[0035]

Table 1]

	放電容量 (mAh/cm ²)	
	初期	300サイクル目
実施例 2	7.4	6.4
比較例 2	5.8	5.2

[0036]The cell of this example 2 is understood that service capacity is large compared with the comparative example 2 so that clearly from Table 1. The theoretical cell capacity in this cell is about 8 mAh/cm^2 , and by the

cell of Example 2, the very near value is shown and it also turns out that it has the outstanding cell performance.

[0037]Change of the service capacity accompanying the charging and discharging cycle of each cell obtained by Example 2 and the comparative example 2 was shown in drawing 2.

[0038]Also in the first stage, the far large thing of service capacity of Example 2 is clearer also in a 300 cycle eye than in drawing 2 as compared with the initial capacity of the comparative example 2. That is, it became producible [a high capacity lithium secondary battery] by containing this lithium-ion-conductivity crystallized glass in an electrolyte.

[0039](Example 3) The lithium secondary battery provided with the compound electrolyte like Example 2 was assembled, and, similarly the charge-and-discharge cycle test under the conditions of the charge final voltage 4.2V and the discharge final voltage 3.0V was done with the application of 3 times as much boost charge in the room temperature of 25 ** as compared with Example 2.

[0040](Comparative example 3) The lithium secondary battery was assembled like the comparative example 2, and, similarly the charge-and-discharge cycle test under the same conditions of the charge final voltage 4.2V and the discharge final voltage 3.0V was done with the application of 3 times as much boost charge in the room temperature of 25 ** as compared with Example 2.

[0041]The measurement result of the initial service capacity of each cell and the service capacity of a 300 cycle eye obtained by Example 3 and the comparative example 3 was shown in Table 2.

[0042]

[Table 2]

	放電容量 (mAh/cm ²)	
	初期	300サイクル目
実施例 3	7.1	5.9
比較例 4	5.4	4.6

[0043]The cell of this example 3 is understood that service capacity is large compared with the comparative example 3, and it also turns out that it has the cell performance outstanding also in boost charge so that clearly from Table 2.

[0044]Change of the service capacity accompanying the charging and discharging cycle of each cell obtained by Example 3 and the comparative example 3 was shown in drawing 3.

[0045]Also in the first stage, the far large thing of service capacity of Example 3 is clearer also in a 300 cycle eye than in drawing 3 as compared with the initial capacity of the comparative example 3.

[0046](Example 4) The lithium secondary battery provided with the compound electrolyte like Example 2 was assembled, and it carried out by changing operating temperature in the charge-and-discharge cycle test under the same conditions of the charge final voltage 4.2V and the discharge final voltage 3.0V. The examination was done at each temperature of -10 **, 0 **, 25 **, 50 **, and 75 **.

[0047](Comparative example 4) The lithium secondary battery was assembled like the comparative example 2, and it carried out by changing operating temperature in the charge-and-discharge cycle test under the same conditions of the charge final voltage 4.2V and the discharge final voltage 3.0V. The examination was done at each temperature of -10 **, 0 **, 25 **, 50 **, and 75 **.

[0048]Change of the value of the initial service capacity to the operating temperature of each cell obtained by Example 4 and the comparative example 4 was shown in drawing 4.

[0049]Even if the cell of Example 4 maintains big service capacity in -10 ** to 75 **, and a wide temperature requirement and measures it with the comparative example 4, its excelling far is clearer than drawing 4.

[0050](Example 5), without using the used hexafluoropropylene HFP as a plasticizer at the time of production of a medium, Each granular material of polyvinylidene fluoride (PVdF) and lithium-ion-conductivity crystallized glass is similarly used as acetone suspension with the mass ratio of 60:40, The lithium secondary battery provided with the compound electrolyte like Example 2 was produced except having produced the sheet-shaped crystallized glass composite medium. The amount of being impregnated of the nonaqueous electrolyte was about 18% of the mass of the compound electrolyte.

[0051](Comparative example 5) At the time of production of a medium, the cell was produced like Example 5 except having added an equivalent amount of powdered fumed silica (SiO₂) by which surface ornamentation was carried out instead of the lithium-ion-conductivity crystallized glass granular material.

[0052]In the cell of Example 5 and the comparative example 4 which are not using the hexafluoropropylene (HFP)

which was being used as a plasticizer. In both cases, the impregnating ability of the electrolysis solution was bad and had only the rate of impregnation of about 30 percent as compared with the cell of Example 4 and the comparative example 4 which use hexafluoropropylene (HFP).

[0053] Change of the value of the initial service capacity to the operating temperature of each cell obtained by Example 5 and the comparative example 5 was shown in drawing 5.

[0054] The cell of the comparative example 5 which contains an electrolysis solution only about 30 percent as compared with the comparative examples 2-4 showed only very small service capacity. In the cell of Example 5 which contains an electrolysis solution only about 30 percent in a similar manner compared with it, service capacity high enough was shown, it was almost equivalent to the comparative example 4, or the capacity beyond it was obtained. This is based on the predominance of the lithium-ion-conductivity crystallized glass which the compound electrolyte was made to contain. That is, also in the case where the rate of the electrolysis solution which is an organic liquid component in a lithium secondary battery is reduced, it has suggested that manufacture of a cell with service capacity high enough is possible, and the lithium secondary battery which was further excellent in safety as a result can be manufactured.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a section explanatory view showing the internal structure of the lithium secondary battery provided with the crystallized glass compound electrolyte in Example 2.

[Drawing 2]It is a graph which shows change of the service capacity accompanying the charging and discharging cycle of each cell obtained by Example 2 and the comparative example 2.

[Drawing 3]It is a graph which shows change of the service capacity accompanying the charging and discharging cycle of each cell obtained by Example 3 and the comparative example 3.

[Drawing 4]It is a graph which shows the initial service capacity to the temperature conditions of each cell obtained by Example 4 and the comparative example 4.

[Drawing 5]It is a graph which shows the initial service capacity to the temperature conditions of each cell obtained by Example 5 and the comparative example 5.

[Description of Notations]

1: Positive pole collector

2: Anode

3: Crystallized glass compound electrolyte

4: Negative electrode

5: Negative pole collector

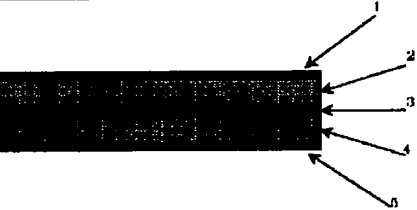
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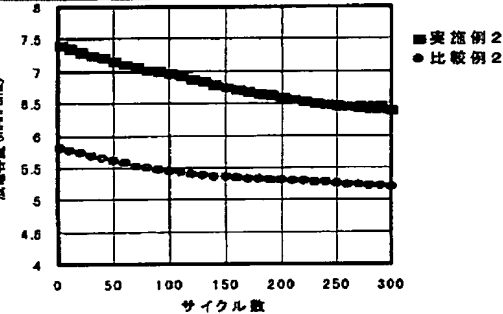
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DRAWINGS

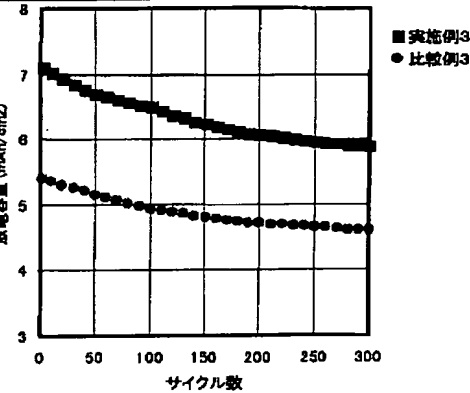
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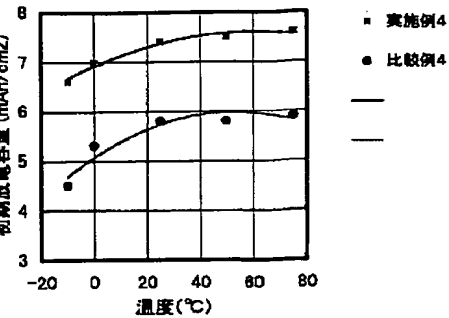
Drawing 2]



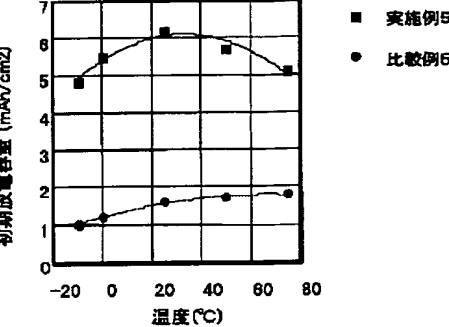
Drawing 3]



Drawing 4]



Drawing 5]



[Translation done.]